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(54) POSITIVE ELECTRODE FOR LITHIUM SECONDARY BATTERY, AND LITHIUM SECONDARY BATTERY USING THEREOF

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a positive electrode for lithium secondary battery, which has a high energy density and which restrains fuse-out and decomposition of the electrolyte by carrying a layer, which includes the active material, in a plate-like collector coated with a layer including InO2, which is doped with Sn, or SnO2 in a surface of a collector substrate.
SOLUTION: A layer including the active material is carried by a plate-like collector so as to obtain a positive electrode for lithium secondary battery. This collector is formed by coating a surface of the collector substrate with a layer, which includes ITO or SnO2, at 0.01-10 μm of thickness. This collector substrate is obtained by coating a surface of a non-conductive sheet such as glass and plastic with Au, Ag, Pt, Cu, Zn, Pb, Ni, Al, Cr, Ti, Sn, Fe at 10-200 μm of thickness, and internal resistance of a battery is desirably lowered. The layer, which includes ITO and SnO2, is desirably formed of ITO, SnO2 fine grains having a grain diameter at 3-50 μm and matrix such as polymer and glass.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the charge of rechargeable battery material, especially a lithium secondary battery positive-electrode object.
[0002]
[Description of the Prior Art] In recent years, the air pollution substance for the large electric vehicle of expectation is not discharged as a substitute of the automobile using the gasoline engine or the diesel power plant, but to environment, as a power supply for portable devices, such as a low driving source of a degree of contamination, and a camcorder/movie, a CD player, a note type computer, a cellular phone, it is small and lightweight and waits for development of the rechargeable battery of high-energy density. Furthermore, it stores in the rechargeable battery which installed power in ordinary homes etc. night as a method of using effectively the power made in plant, and the rechargeable battery of high-energy density is called for also in the so-called load leveling (load leveling) use of using this for daytime with much power consumption.
[0003] $LiCoO_2$ which introduced the lithium ion into the intercalation compound as a cell which meets such a demand, for example etc. -- the rocking-chair type lithium secondary battery which used carbon system material, such as graphite, is developed and marketed by the negative-electrode active material in the oxide at the positive active material Since this lithium secondary battery has charge and discharge potential (about 4 V) higher than a conventional rechargeable battery like a nickel hydoride battery (about 1.5 V) or a lead accumulator (about 2 V), the composition member of cells, such as the electrolytic solution, a positive/negative pole, separator, and a cell case (sheathing can), is **(ed) by the severer oxidation reduction state, and higher anti-oxidation reducing and higher stability are required.
[0004] The positive electrode which added electric conduction supplement agents, such as acetylene black, as a positive electrode (positive electrode) which fills this demand if needed [a fluorine system resin or if needed] as a binder to the active material, produced the paste, and applied this paste to the charge collector is common. Therefore, although a moderate mechanical strength is required of a charge collector, if thickness of a charge collector is enlarged not much, the volume which a charge collector occupies within a cell case will become large, consequently the fill of an active material decreases, and the charge-and-discharge capacity of a cell falls.
[0005] On the other hand, since an electron is supplied to the active material of a positive/negative pole in order to neutralize electrically the reaction by the dope into the active material of electrolyte ion, and the ** dope, or it has the duty which takes out the spark discharge energy of a cell outside in a charge collector, high electronic-conduction nature is required. Therefore, if thickness of a charge collector is made not much thin, an electric resistance value will become high, the internal resistance of a cell increases, and charge-and-discharge efficiency falls. Furthermore, for example, elution into the electrolytic solution of a positive-electrode charge collector metal arises at the time of the charge from which a positive electrode serves as high potential, and the problem that cell capacity falls arises as indicated by the open patent common No. 290854 [five to].
[0006] With the commercial lithium secondary battery, the aluminium sheet is adopted as the positive-electrode charge collector that an above-mentioned problem should be solved. The rate of an electronic conduction of aluminum is high, and its electrochemical stability is high, maintaining high electronic-conduction nature, in order to excel in processability and to form an oxide film in a front face still more easily.
[0007]
[Problem(s) to be Solved by the Invention] However, if the cell voltage of the above-mentioned lithium secondary battery is set to about 4v or more by the surcharge by misuse etc. even if it is the positive-electrode charge collector of aluminum, aluminum is eluted in the electrolytic solution or it is known widely that will disassemble the solvent of the electrolytic solution, will generate gas and the internal pressure within a cell case will rise (for example, the volume Masayuki Yoshio and for Akiya Ozawa, a "rechargeable lithium-ion battery", the Nikkan Kogyo Shimbun Ltd. issue, 1996). In order to prevent this phenomenon, in the commercial lithium secondary battery, the circuit which detects a surcharge and is protected quite strictly is needed, and the relief valve for missing the gas which the electrolytic solution decomposes and occurs is prepared.
[0008] When the circuit for detection of the surcharge of the lithium secondary battery of these marketing and protection and installation of a relief valve not only become a cost rise, but have the need of preparing in a cell case, they need the capacity of exclusive use, they reduce the energy density of a cell, and are not desirable for the smaller and lightweight use searched for.
[0009] In the lithium secondary battery in a overcharge state, although covering an aluminum oxide on the front face of the aluminum of a positive-electrode charge collector, and making it a charge collector metal and the electrolytic solution not contact

is proposed in order to suppress elution into the electrolytic solution of a positive-electrode charge collector, and decomposition of the electrolytic solution (JP,4-237955,A), an aluminum oxide has a possibility that the electronic conduction of a charge collector and an active material may be spoiled, and charge-and-discharge efficiency may fall so highly [conductivity]. Moreover, the tantalum is indicated as a charge collector metal which fills such a demand by JP,5-290854,A. However, since the processability and mechanical property of a tantalum are strongly influenced of the impurity element of a minute amount, it is necessary to pay careful attention of performing the manufacture in an argon air current, and cannot be called the cell material which was cheap compared with aluminum and was excellent in processability (a "metal handbook", the edited by Japan Institute of Metals, the Maruzen Co., Ltd. issue, 1982).

[0010] this invention aims at offering the lithium secondary battery with the long cycle life of charge and discharge using the positive-electrode charge collector of the lithium secondary battery which suppresses elution into the electrolytic solution of the charge collector by the surcharge, and decomposition of the electrolytic solution, and this, without solving the technical problem of the aforementioned conventional technology and reducing the energy density of a cell.

[0011]

[Means for Solving the Problem] In the lithium secondary battery positive-electrode object containing the tabular charge collector which supports the layer and this in which this invention contains an active material, the aforementioned charge collector is a lithium secondary battery positive-electrode object characterized by the bird clapper from the layer containing the indium oxide or the tin oxide which was covered by a charge collector substrate and its front face, and which doped tin.

[0012] In this invention, the layer containing the layer which contains the indium oxide (ITO) which doped tin in the current collection body surface of the positive electrode in which a lithium ion and reversible electrochemical reaction are possible, a negative electrode, and the aforementioned positive electrode used for the lithium secondary battery which consists of lithium ion content nonaqueous electrolyte, or a tin oxide is coated. It is a tin oxide (SnO_2) here. The tin oxide in the included layer may be doped with small quantity, for example, 0.1 - 2% of the weight of a fluorine, boron, antimony, etc. Although the layer containing the layer containing ITO or a tin oxide may be a layer of the simple substance of ITO or a tin oxide, you may be the layer which consists of an ITO particle (or tin-oxide particle) and a matrix. The polymer or glass like polyester resin as this matrix is used. A matrix makes the front face of a positive-electrode charge collector substrate fix an ITO particle or a tin-oxide particle, and the layer which consists of an ITO particle (or tin-oxide particle) and a matrix carries out the duty which maintains an electric flow with an active material and a charge collector substrate. Moreover, as an ITO particle or a tin-oxide particle, what has the diameter of 3nm (0.003 micrometers) - 50nm (0.05 micrometers) is used preferably.

[0013] SnO_2 and ITO which are a typical n type oxide semiconductor, It excels in electrochemical oxidation resistance, and in nonaqueous electrolyte like a lithium secondary battery, the conductivity is comparatively as high as about $10Scm^{-1}$, and the oxygen overvoltage is high, and it is [it is stable and] suitable as a material which coats the current collection body surface which touches the electrolytic solution at least.

[0014] It sets to this invention and is SnO_2 on the charge collector substrate of a positive electrode. or as a method of covering the layer containing ITO (1) After coating the alcoholate of tin, a carboxylate, a halogenide, etc. on a charge collector substrate, A fluorine compound and an antimony compound are mixed with the sol gel process considered as hydrolysis and baking, (2) alkyl tin, halogenation tin, carboxylic-acid tin, etc. The method and (3) SnO_2 which coat this by the pyrolysis spray method or CVD on the charge collector substrate heated beforehand Or ITO compounded beforehand is used as a target. It is SnO_2 on a charge collector substrate to sputtering or the physical method of carrying out vacuum deposition, (4) resins, or a binder. Or although the so-called CLD method which coats the liquid which distributed the particle of ITO on a charge collector substrate by the dipping method or the roll coat method is possible The coating method is chosen according to the kind and configuration of a base material.

[0015] If the thickness of the layer containing Above ITO or a tin oxide is too small not much, decomposition suppression of the electrolytic solution and the effect of prevention of the elution to the electrolytic solution of the charge collector metal by the surcharge will become small, if thickness is too large not much conversely, the occupied volume of the charge collector within a cell case will become large, and the charge-and-discharge capacity of a cell will fall. Therefore, the thickness of the layer containing ITO or a tin oxide has desirable 0.01-1.0 micrometers, and its 0.1-0.5 micrometers are more desirable.

[0016] As a charge collector substrate with which the layer containing Above ITO or a tin oxide is covered, it is desirable to have the thickness of 10-200 micrometers, and it can use glass, an insulator like plastics, and a good conductor like a metal as the material. As a metallic material of a charge collector substrate, in order to make internal resistance of a cell as small as possible, at least one sort of metals or the alloy chosen from the metal of a group which consists of a metal, for example, gold, silver, platinum, copper, zinc, lead, nickel, aluminum, chromium, titanium, tin, and iron is used preferably, and it can choose from these in consideration of affinity with conductivity, processability, cost, and other material etc.

[0017] In using glass and an insulator like plastics as a material of a charge collector substrate In order to make internal resistance of a cell as small as possible, before making the layer containing ITO or a tin oxide cover It is desirable to cover with the thickness of 0.01-10 micrometers at least one sort of metals chosen from the metal of a group which consists of a metal, for example, gold, silver, platinum, copper, zinc, lead, nickel, aluminum, chromium, titanium, tin, and iron, or these alloys. More desirable thickness is 0.1-2 micrometers.

[0018] in this invention, although the layer containing a positive active material is supported by the tabular charge collector, as this positive active material, occlusion and discharge are possible in a lithium ion in reversible $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ etc. -- an oxide, a mixed-valence complex given in application patent common [No. 174453 / eight to], etc. can be used After carrying out proper quantity mixture and making an electronic-conduction nature grant agent like acetylene black, and a binder

like a fluorine system resin into the shape of a paste at this positive active material, it can consider as a positive electrode by applying to a charge collector.
[0019] As a negative-electrode active material in the lithium secondary battery of this invention, carbonaceous material and tin-oxide material can be used for the lithium metal and lithium alloy in which occlusion and discharge are possible in reversible, and a pan for a lithium ion.
[0020] As nonaqueous electrolyte of the lithium secondary battery of this invention, what was usually dissolved in the solvent by the concentration of about one mol / L is used by making lithium salt, such as LiClO4 and LiBF4, into a solute. As a solvent, nitril, such as cyclic ether, such as chain-like ether, such as gamma-lactone, such as carbonates, such as propylene carbonate and ethylene carbonate, and gamma-butyrolactone, and ethoxy methoxyethane, and a tetrahydrofuran, and an acetonitrile, and the mixed solvent of those can be used.
[0021]
[Embodiments of the Invention] Hereafter, although an example explains this invention in more detail, this invention is not limited to these examples, unless the summary is exceeded.
[0022] In order to investigate the decomposition voltage of the [example 1] electrolytic solution, it is SnO2 by CVD to the single-sided front face of a soda lime glass substrate. The electrode which coated ITO by the sputtering method, respectively was produced. The steam which heated monobutyl tin trichloride (C4H9SnCl3, liquid) at 135 degrees C N2 as carrier gas It mixes with gas, carries to a chamber, and is a 60-degree C steam and O2 to this. Gas is added as an oxidizer. The gas which added the chlorofluocarbon (1 and 1 difluoroethane) of a minute amount, and was mixed (by N2;80L/) Sn raw material; the soda lime glass substrate of 1.1mm ** which heated 13 weight sections, the steam 5 weight section, the O2;80 weight section, and the chlorofluocarbon;3.5 weight section at 500-550 degrees C was sprayed, and the electrode which coated the thickness of 0.6 micrometers with SnO2 on the single-sided front face was produced. SnO2 film is SnO2 of a polycrystal. In the shell, F atom was contained about 1%. The surface-electrical-resistance values of this electrode were 20ohm/**. Let this electrode as a working electrode and let lithiums be a counterelectrode and a reference electrode. LiClO4 (electrolyte) fully dried to weight ratio 1:1 mixed solutions of propylene carbonate and dimethyl ethane What was dissolved by the concentration of one mol / L was made into the electrolytic solution, and the trilateral formula cell was produced in the glow box which carried out argon substitution. About this trilateral formula cell, the cyclic voltamogram was measured at 10mV [/second] sweep speed. A dotted line 1 shows the result to drawing 1 . drawing -- setting -- a vertical axis -- the oxidation reduction current per working-electrode unit area (A/cm2) -- a horizontal axis shows the potential (V) of the working electrode to a reference electrode When the potential of a working electrode was changed to +2.5-+5.0V on the basis of the lithium electrode, decomposition of the electrolytic solution was not accepted in about 4.5v or less. And oxidation reduction current is 1x10-5 A/cm2. The potential of the working electrode at the time of the working-electrode rise when becoming was about 4.7V. Moreover, change was not accepted in the resistance and appearance of the above-mentioned electrode after cyclic voltamogram measurement.
[0023] Moreover, sputtering of the ITO was carried out to the single-sided front face of the soda lime glass substrate of 1.1mm **, and the electrode with which the ITO film of 200nm ** was covered was obtained. The surface-electrical-resistance values of this electrode were 10ohm/**. The cyclic voltamogram was measured for this electrode like the example 1 to the operation pole. A solid line 2 shows the result to drawing 1 . Decomposition of the electrolytic solution was not accepted up to the 4.5V neighborhood to the lithium electrode like the above.
[0024] It pulled up, after flooding with the solution (GIP-In500 made from **** Science EA) which dissolved in alcohol the indium oxide alcoholate which doped tin for the aluminium sheet of [example 2] 25-micrometer **, and under nitrogen atmosphere, it calcinated at 450 degrees C for 20 minutes, and the aluminum electrode by which the front face was coated with ITO was obtained. The thickness of the covered ITO film was 0.2 micrometers. The surface-electrical-resistance value of the ITO film of the same thickness which performed and measured the processing same as a monitor as a soda lime glass substrate was 3Kohm/**. And not increasing, after the resistance of an aluminum electrode covers the above-mentioned ITO film was checked. This electrode was used as the working electrode and the cyclic voltamogram was measured by the same method as an example 1. A dotted line 3 shows the result to drawing 2 . Less than [4.8V], decomposition of the electrolytic solution was not observed to the lithium electrode.
[0025] After washing the soda lime glass substrate of [example 3] 1.1mm ** in a penetrant remover (; made from Okuno Pharmaceuticals " KONDI clean OPC380"), and the hydrochloric-acid solution of pH=2, nickel-plating processing was performed as follows. First, 0.1g of two hydrates of chlorination tin was dissolved in pure water 1L, and the glass substrate finishing / the above-mentioned washing] was flooded with the solution which added 0.1 cc of hydrochloric acids for 2 minutes, then it flooded with the solution which dissolved 0.1g of palladium chlorides in pure water 1L, and added 3.5 cc of hydrochloric acids for 2 minutes. 150 cc (product made from Okuno Pharmaceuticals "TMP HR-TA") of non-electrolyzed nickel plating liquid and 150 cc (product made from Okuno Pharmaceuticals "TMP HR-TB") of non-electrolyzed nickel plating liquid were put in into 700 cc pure water, and it mixed, and to this, the 25-% of the weight aqueous ammonia solution was added so that it might be set to pH=9 of liquid, and the electroless deposition liquid of nickel of 35 degrees C of solution temperature was prepared to it. Glass [finishing / above-mentioned being palladium-chloride immersed] was immersed in the bath of this plating liquid for 7 minutes. After the processing end fully washed the sample with pure water. The obtained sample was dried under the vacuum of 1 or less torr at 80 degrees C for 48 hours. The front face of this glass sample was uniformly coated with nickel by the thickness of about 0.4 micrometers.
[0026] This nickel covering glass plate was pulled up after flooding with the resin solution (Sumitomo Osaka Cement make) of the polyester system which the ITO particle with a diameter of about 0.01 micrometers distributed, under nitrogen atmosphere, it

calcinated for 20 minutes and 160 degrees C of nickel electrodes which ITO pasted up by polyester resin and were covered by both the front faces of a nickel covering glass plate were obtained. The thickness of the covered ITO film was 0.1 micrometers. The surface-electrical-resistance value of the ITO film which performed the processing same as a monitor as a soda lime glass substrate was 3Kohm/**. And there was no change in the resistance of the nickel electrode by the existence of covering of an ITO film. This electrode was used as the working electrode and the cyclic voltamogram was measured by the same method as an example 1. A solid line 4 shows the result to drawing 2 . Less than [4.8V], decomposition of the electrolytic solution was not observed to the lithium electrode.
[0027] The aluminium sheet of [example 1 of comparison] 25-micrometer ** was used as the working electrode, and the cyclic voltamogram was measured like the example 1. A solid line 5 shows the result to drawing 3 . Decomposition of the electrolytic solution is observed from near about 3.8v to a lithium electrode. And oxidation reduction current is 1x10-5 A/cm2. The potential of the working electrode at the time of a working-electrode rise when becoming was about 4.0V. Moreover, as a result of measuring a cyclic voltamogram like the above using the aluminium sheet which made the front face cover an aluminum oxide with a thickness of about 20nm by replacing with the above-mentioned aluminium sheet and heating an aluminium sheet at 500 degrees C for 30 minutes, decomposition of the electrolytic solution is observed from near about 4.0v.
[0028]
[Effect of the Invention] The charge collector which covered ITO and the tin oxide which are an oxide semiconductor can suppress the generation of gas by the fall of the charge-and-discharge capacity which originates in elution into the electrolytic solution of the charge collector metal by the surcharge since it is stable in the electrolytic solution of a lithium secondary battery and decomposition of the electrolytic solution can be suppressed up to the 4.5V neighborhood to a lithium electrode, and decomposition of the electrolytic solution, and a more reliable lithium secondary battery positive-electrode object is acquired as explained above.

[Translation done.]